

AMORPHOUS MINERALS AND CONTROL OF THE CHEMICAL COMPOSITION OF SOIL SOLUTIONS

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In order to assess whether amorphous minerals - water interaction can be accounted for in terms of heterogeneous equilibria, it is necessary to distinguish between constant composition or variable composition minerals. For the former, dissolution and newformation proceed along a well defined stoichiometry. Differences between more or less soluble phases can be ascribed to particle size and/or crystallinity, and eventually to excess surface free energy.

For the latter, solid solution formalism implies to write a particular equilibrium relationship for each end-member of the solid solution, which allows to use the independently determined data for the pure amorphous end-members, altogether with either ideal solid solution or regular solid solution hypotheses. It must be underlined that one may not write an equilibrium relationship for a mineral whose stoichiometry is not fixed, as in this case the chemical potential of the solid is not defined. On the contrary, for each end-member, the chemical potential has a definite value. The variables are then the proportions of the different end-members in the solid solution.

Elements that form amorphous minerals are mainly Si, Al, Fe as oxides, hydroxides and sulphides. Those elements are generally present in solution as not only mononuclear species, but also as polynuclear (or polymeric) species. When computing ion-products from the analysis of the solution, one must be aware of the necessity to consider that a non negligible part of the dissolved element may be present as polynuclear species. This is of special significance for Al.

Moreover, high concentrations of electrolytes were shown by MARSHALL et al. to decrease the solubility of amorphous silica, according to the classical Setchenow's law for "salting-out" effect. Activity coefficient of aqueous silica is thus more sensitive than previously expected to ionic strength. The previous considerations allow to check equilibrium between amorphous SiO_2 - Al_2O_3 , product ("allophane") considered as an ideal solid solution and natural waters, using the classical equilibrium diagrams, in which stability fields of constant composition minerals are bound by straight lines, whereas ideal solid solution is bound by a curve.

Spring waters from acidic brown soils on granite, in Fougères (Armorican Massif) appear to be undersaturated with respect to amorphous ideal solid solution in the Al_2O_3 - SiO_2 - H_2O system and aluminium is more likely to be controlled by gibbsite.

In addition to their own newformation, a possible geochemical role of amorphous minerals is a protective role of coatings on dissolving primary minerals or of amorphised surface layers of those minerals themselves. Kinetic studies show that this mechanism is not significant and that amorphous mineral coatings are not likely to limit proton or ion transfer. Moreover, amorphous layers resulting from the collapse of the surface layers of the primary minerals are not thick enough to play a role. The essential geochemical role of amorphous minerals is thus to modify the chemical conditions in the milieu by controlling Si, Al, Fe or the pH, more than to constitute a physical barrier to diffusion processes.

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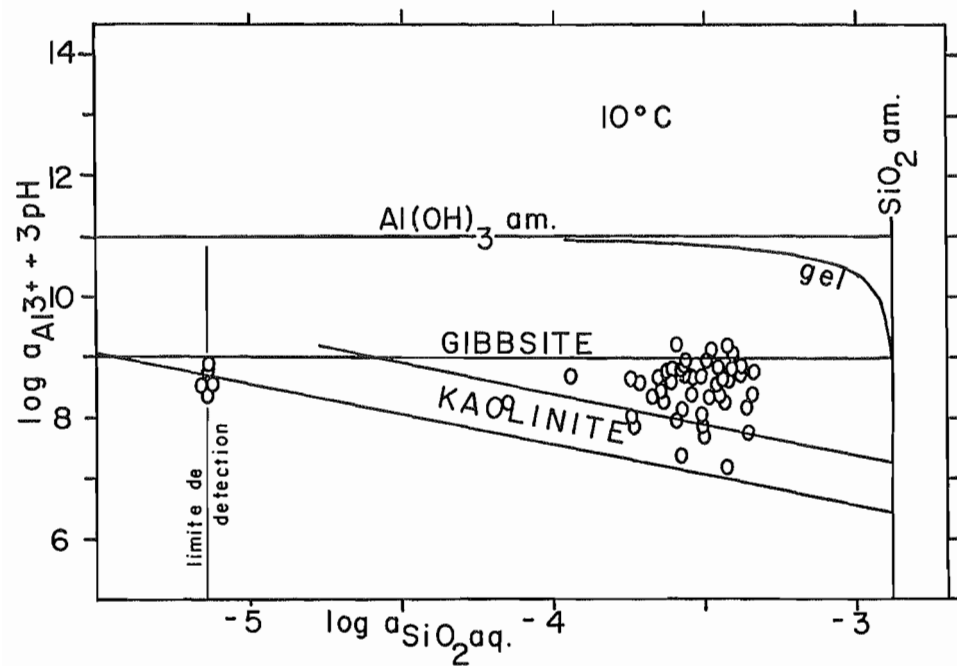


Figure 4 : Phase diagram of the system $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-H}_2\text{O}$ at 10°C, 1 bar. Dots indicate the chemical composition of spring waters from Fougères (Armorican Massif), computed with provision for the existence of a polynuclear complex of dissolved Al.